Inclusions in Silver Voltameter Deposits and the Electrochemical Equivalent of Silver

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A DISSERTATION

PRESENTED TO THE FACULTY OF PRINCETON UNIVERSITY IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF SCIENCE

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WILLIAM MILLER BOVARD

EASTON, PA.:
ESCHENBACH PRINTING CO.
1917

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Introduction.

The extensive and painstaking work which has been done on the silver voltameter has established the fact that it is reproducible to one or two parts in a hundred thousand and is the best standard as yet devised for the measurement of quantity of electricity. The relation between the coulomb and the weight of silver deposited from a silver nitrate solution is known to a high degree of precision when certain arbitrary specifications[1] are followed, but this figure does not necessarily represent the true electrochemical equivalent of silver. The inclusions in the deposited

* The work described in this article was made possible by a grant from the Elizabeth Thompson Science Fund, which placed at our disposal some of the special apparatus and materials needed for this investigation. The authors take pleasure in acknowledging their indebtedness to the Trustees of this Fund.

[1] Bur. Standards, *Bull.* 13, 499 (1916).

silver should certainly be taken into account and furthermore it must be known whether any other reactions than the one $Ag^+ \longrightarrow Ag$ play a measurable role in carrying the current from electrolyte to cathode.

Hitherto very little attention has been paid to the question of secondary reactions at the cathode and almost all of the work on the silver voltameter has been either an endeavor to make it a reproducible instrument or an investigation as to the inclusions in the deposited silver. There are many reactions which might take place and possibly affect the weight of the deposits. Thus there is some evidence of silver in a lower state of oxidation[1] and if such an ion exists in the solution, the change $Ag^+ + Ag \longrightarrow Ag_2^+$ might take place and give light deposits analogous to the well-known case of copper.

It is also true that hydrogen ions are present in the solution to the extent of 10^{-5} g. equivalents per liter since the electrolyte is one part in a million acid using methyl red as an indicator according to the specifications of the Bureau of Standards.[2] The current goes by all possible paths proportional to the concentration of the ions at the cathode and the decomposition potentials. A deposition of hydrogen according to this view would affect the weight of silver deposited although it may not be to a measurable extent.[3] It is also well known that any positive colloid such as colloidal silver is supposed to be,[4] would migrate to the cathode and be deposited. The current carried by these particles would be much less than for the same amount of silver in the forms of ions. There is also the possibility that a complex ion, if formed at the anode, would reach the cathode and affect the weight of the deposited silver. It is therefore of importance to know whether the silver deposited is in accordance with the simple reaction $Ag^+ \longrightarrow Ag$ or whether these secondary reactions play a measurable role.

The simplest method of investigation seemed to be to compare the anode loss and cathode gain. Of course, reactions might take place at the anode, such as the formation of a complex ion of silver in a higher state of oxidation or the discharge of OH^- or O^{--} ions. The concentrations of these ions are smaller than the concentration of H^+ because of the displacement of the equilibrium by the small amount of acid present. However, all of these reactions, with the exception of the improbable discharge of oxygen, would lessen the weight of the anode and therefore increase the anode loss, so that there would be even a greater divergence between the anode loss and the cathode gain. Thus, if pure silver be used as an anode and if the weight of the deposited silver on the cathode be corrected for

[1] Dammer's "Handbuch der Anorganischen Chemie," **2**, 767; Thorpe's, "Dictionary of Applied Chemistry."

[2] Bur. Standards, *Bull.* **9**, 529 (1912); **10**, 502 (1913).

[3] *Ibid.*, **10**, 507 (1913).

[4] *Ibid.*, **9**, 220 (1912).

inclusions, then a comparison of the anode loss and cathode gain should show the presence or absence of any influence that would make the weight of deposited silver deviate from the correct weight corresponding to Faraday's law. This would enable the electrochemical equivalent of silver to be calculated with certainty. It might also throw some light on the present discrepancy between the silver, iodine, and cadmium voltameters.[1] The present communication records the results of work which was performed, firstly, to compare the anode loss and cathode gain and to determine the inclusions in the latter and, secondly, to ascertain the value of the inclusions in electrolytic silver as deposited in a standard platinum cup voltameter. During the work a special form of voltameter was devised to compare the anode loss and the cathode gain. The inclusions in the deposits in this form of apparatus and also in deposits on a silver cup voltameter were determined.

I. Comparison of the Anode Loss and Cathode Gain.

Very little attention has hitherto been paid to the question of anode loss and cathode gain. The comparison was first determined by Mascart in 1882[2] and later by Gray in 1886,[3] but the accuracy of their work was such that no conclusions can be drawn regarding small secondary reactions. In 1892 Novak,[4] using a small voltameter of the Kohlrausch form, experimented on the loss at the anode, the gain at the cathode, and the change in the concentration of the electrolyte. He collected the "anode slime" on filter paper, dissolved it in nitric acid and weighed as silver chloride. The concentration of the electrolyte before and after the run was determined by precipitation with hydrochloric acid. As a result of six determinations, he concluded that the anode loss was greater than the cathode gain by 162 parts in 100,000, not correcting the cathode gain for inclusions. He also found that the electrolyte decreased in silver content to the extent of 371 parts of silver per hundred thousand of deposit and he therefore assumed that the silver went over into a form not precipitated by hydrochloric acid and that some secondary anodic reaction had occurred. This work, however, was done before the silver voltameter had been brought to its present state of perfection. On the other hand, Guthe[5] showed that the total concentration of the silver nitrate solution remained unchanged during the electrolysis and he could not find evidence of a complex ion.

In 1902, Richards and Heimrod determined the anode loss and cathode

[1] Vinal and Bates, Bur. Standards, *Bull.* **10**, 425 (1913); Laird and Hulett, *Trans. Am. Electrochem. Soc.*, **22**, 385 (1912).

[2] Mascart, *J. Physique*, **1**, 109 (1882); **3**, 283 (1884).

[3] Gray, *Phil. Mag.*, **22**, 389 (1886).

[4] "Studie o voltametru na stribo," *Proc. Roy. Bohemian Acad. Sci. Prague*, **1**, 387–432 (1892).

[5] Guthe, Bur. Standards, *Bull.* **1**, 355 (1905).

gain in a porous pot, platinum cup voltameter, collecting the anode slime in a Gooch crucible.[1] Their seven determinations vary from +70 to —54 parts per 100,000 and give as a mean value that the anode loss is greater than the cathode gain by 12 parts. They did not correct the cathode deposit for inclusions, which they found to be 18 parts per hundred thousand in other similar deposits. The total difference between the anode loss and cathode gain is thus 30 parts per hundred thousand. As a result of several lines of evidence, they were of the opinion that the heavy complex ion mentioned by Novak plays an important role in the silver voltameter and that the anode loss does not equal the cathode gain.

More recently, Rosa, Vinal and McDaniel[2] used a reversible voltameter of the siphon form with a silver deposit on platinum as the anode. This form gave practically no anode slime. Two determinations showed that the anode loss exceeded the cathode gain by 1.2 and 9.6 parts per hundred thousand, assuming that the inclusions in the anode were the same as in the cathode deposit. Their results give a closer agreement between the anode loss and cathode gain than any of the previous work, but there were only two determinations and the conditions of the run were not quite the same as in the standard voltameter.

In none of the above researches were the inclusions in the actual deposits determined and thus the amount of pure silver deposited on the cathode and dissolved at the anode has never been compared. For our experiments a new form of voltameter was devised to enable the amount of pure silver in the actual deposits to be determined. It had previously been found by Hulett that silver deposited from a silver nitrate solution on a highly polished silver surface can be readily detached. By thus separating the crystals from the cathode before weighing and then determining the inclusions in the same sample, a correct value for the amount of pure silver deposited can be obtained. A comparison of this deposit with the deposit in a standard platinum cup voltameter would show the relation of this deposited pure silver to that according to standard specifications.

A. **Apparatus.**—The form of voltameter finally adopted was a modification of the Smith form,[3] a type which was found to agree with the platinum cup, porous pot form to one part in a hundred thousand.[4] It consisted of two Jena glass dishes made by cutting off two beakers and making a lip on them. The smaller one of 55 mm. diameter and 35 mm. high was placed inside of the larger which was 11 cm. in diameter and 6 cm. high. Over this was placed a cover, through which three holes had been ground. Into the large hole at the center of the cover there slipped

[1] *Proc. Am. Acad. Arts and Sci.*, **37**, 434 (1902).
[2] Bur. Standards, *Bull.* **10**, 499, 528 (1913).
[3] *Nat. Phys. Lab.*, **1910**, 32.
[4] Bur. Standards, *Bull.* **10**, 485 (1913).

a glass cylinder 4.8 cm. in diameter and 5 cm. high and flanged at the top so that when in place it passed inside of the smaller dish to within 25 mm. of the bottom. The anode slime either floated on top or sank to the bottom and was thus kept away from the cathode compartment. The other two holes through the cover were 5 mm. in diameter and served for the passage of the cathode wire and for pipetting out the electrolyte after the run. The parts of the anode and cathode which served to conduct in the current were protected from electrolytic action by two glass tubes which slipped over them. Two glass plates, notched to allow for the anode, were finally placed over the inner compartment to protect it.

The cathode was an Archimedes spiral of polished silver wire 1.45 mm. in diameter, 65 cm. long and having an area of 30 sq. cm. It was made from the purest silver such as was used for the anodes, drawn down by means of draw plates, the surface cleaned with nitric acid and then highly polished by continued rubbing with hardened filter paper. The anodes were made of silver that had been made according to the method used by Hulett and Buckner.[1] Silver chloride was digested with aqua regia, thoroughly washed, dissolved in ammonia water and precipitated with a solution of sugar and caustic potash. This silver was washed, fused in porcelain and poured into water. It was then dissolved in redistilled nitric acid, having an excess of silver present, and was finally precipitated by ammonium formate.

This silver was fused in porcelain, cast in graphite moulds, the surface dissolved in nitric acid and was then drawn down to 3 mm. diameter. In drawing to wire it was annealed either in a clean hard glass tube externally heated or in an alcohol flame free from injurious gases. One end of this wire, which was 12 cm. in length, was then bent into a shape resembling the letter G, 25 mm. in diameter, the remainder of the wire being bent at right angles. Connection to a silver wire of 1.45 mm. diameter was made by slotting the end of the wire (which during the run was 2 cm. above the electrolyte) and then closing up the slot after inserting the keystone-shaped end of the smaller wire.

The silver nitrate used in these runs was made according to the Princeton method[2] and fused in quartz. It conformed to the specifications of the Bureau of Standards that it shoud not be more than 2 nor less than 0.5 parts per million acid, using methyl red as an indicator, and that 10 g. of a 66% solution plus 1 cc. conc. nitric acid should not decolorize 1 cc. of a permanganate solution 0.001 *N* in less than 5 minutes.[3] It was always filtered before use through a platinum Neubauer crucible similar to, but not one of, the crucibles used in the determination.

[1] *Trans. Am. Electrochem. Soc.*, **22**, 372 (1912).
[2] Hulett and Buckner, *Ibid.*
[3] Bur. Standards, *Bull.* **9**, 529, 531 (1912).

Platinum Neubauer crucibles were used to collect the anode slime and the cathode crystals. These crucibles were previously ignited, soaked in strong caustic potash, then in concentrated nitric acid, washed, and finally a large amount of 10% silver nitrate solution filtered through. They were tested for constancy in weight by filtering electrolyte through them and reweighing and although they were not as constant as had been hoped, yet their variation would not affect the comparison of the anode loss and cathode gain by more than one part per hundred thousand.

Crucible.	Treatment.	Change in weight.
C (used for cathode)	200 cc. 10% $AgNO_3$ and 200 cc. water.....	+0.005 mg.
C (used for cathode)	200 cc. 10% $AgNO_3$ and 200 cc. water.....	+0.01
C (used for cathode)	200 cc. 10% $AgNO_3$ and 200 cc. water.....	—0.05
C (used for cathode)	200 cc. 10% $AgNO_3$ and 200 cc. water.....	+0.05
A (used for anode)	200 cc. 10% $AgNO_3$ and 200 cc. water.....	+0.00
A (used for anode)	200 cc. 10% $AgNO_3$ and 200 cc. water.....	—0.045
C (used for anode)	200 cc. 10% $AgNO_3$ and 200 cc. water.....	—0.032
		Mean, —0.009

Before each run they were cleaned successively with nitric acid, conductivity water, silver nitrate solution and finally conductivity water. They were then heated to 160° for an hour as in the procedure employed after the deposition of the silver.

The platinum cup standard voltameters are the same instruments as were used in all of the previous Princeton work and at the Bureau of Standards.[1] The platinum cups have an area of 150 sq. cm. and a capacity of 165 cc. The porous pots were prepared by soaking first in strong caustic potash solution and then in concentrated nitric acid. Conductivity water was then allowed to percolate through the cups over night with a siphon arrangement, and then 10% silver nitrate solution was passed through.

All the weighings were done on a Rueprecht balance of 200 g. capacity, in a balance room of constant temperature and humidity. The weighings, which were accurate to 0.02 mg., were carried out by a modification of the Borda method. The silver anode, Neubauer crucible *A* and a small amount of silver to make the weight of this combination equal to the cathode combination, were balanced against a tare of the same amount of platinum and silver, first with the rider on 1 mg. and then with the rider off. The pans were then interchanged and the balance again determined. The cathode wire and Neubauer crucible *C* were then substituted for the anode, anode crucible and tare and similar readings taken. By this method, a comparison of the anode combination and of the cathode combination could be had with the tare and also three checks of the rela-

[1] Duschak and Hulett, *Trans. Am. Electrochem. Soc.*, **12**, 257 (1907); Buckner and Hulett, *Ibid.*, **22**, 369 (1912); Hulett and Vinal, *J. Phys. Chem.*, **19**, 176 (1914); Vinal and Bovard, *J. Am. Chem. Soc.*, **38**, 496 (1916).

tion between the anode combination and the cathode combination to show the accuracy of the observations. After the run, a silver slug equal to the weight of silver deposited[1] was added to the anode to take the place of the silver dissolved and added to the tare when the cathode was weighed. From these relations to the tare, the anode loss and cathode gain were calculated.

In making a run, the cathode was held just clear of the bottom of the dish by means of a clamp and the anode was adjusted so that it was on the same level as the bottom of the inside cylinder. The electrolyte of 10% silver nitrate solution was added so as to cover the top of the small dish to a depth of 2 cm. The platinum cup voltameters were placed in series and a current of 0.3 ampere used. After deposition the electrolyte was removed to below the top of the inside cup by means of a special pipet which could be inserted between the inside cup and the cylinder. The solution was withdrawn slowly and always examined for loose silver. The anode was then placed in the Neubauer crucible, the anolyte filtered through and the inside cup thoroughly washed. The anode slime was thus transferred with the aid of the wash waters into the crucible and finally washed with conductivity water until the filtrate showed no sign of turbidity after the addition of a drop of nitric acid and potassium bromide. The cathode was thoroughly washed and in order to avoid inclusions between the crystals and the silver wire, the deposit was detached with a glass rod. The glass rod was always examined after this process and did not suffer to an appreciable extent. Finally, the crystals were transferred to the crucible and the whole well washed. The crucibles, anode and cathode wire were heated to 160°, cooled in a desiccator and weighed. After the calculation of the anode loss and the cathode gain the deposit was transferred to a clean dry tube, sealed and subsequently used for a determination of the inclusions.

B. **Results.**—The results of the anode loss and cathode gain determinations, the majority of which were carried out in conjunction with Mr. F. M. Seibert, are given in Table I, the inclusions in the cathode deposits having been determined later in the present work. The value for the amount of the inclusions in the deposit on platinum is taken as that found from similar deposits on platinum also determined later. The experiments have been critically reviewed from many points of view and there is no knowledge of any abnormality except in Runs 9, 10 and 11, which were not included in the average value. Runs 10 and 11 were made with electrolyte from the same fused silver nitrate and the acidity was unfortunately not determined in these runs. These two results are obviously

[1] A gold-plated silver weight (4.09824 grams as determined by the Bureau of Standards) was used and during the run this amount of silver was deposited as nearly as could be done by noting current and time.

TABLE I.

Run No.	Date. 1915.	Deposits on Pt cups. G.	Cathode gain. G.	Anode loss. G.	Cath. gain minus anode loss. Mg.	Cath. gain minus Pt. cups. Mg.	Pt. cups minus anode loss. Mg.	Parts in 100,000. Cath. gain minus anode loss.	Cath. gain minus Pt cups.	Pt. cups minus anode loss.	Inclusions in cath. gain.	Inclusions in deposit on Pt.	Corrected for inclusions. Cg–A1.	Cg–Pt.	Pt–A1.
5	Apr. 1	4.18632													
		4.18634													
		4.18633	4.18703	4.18685	0.18	0.70	—0.52	4.3	16.7	—12.4	12.3	...	—8.0	11.1	—19.1
6	Apr. 8	4.13388													
		4.13384													
		4.13386	4.13422	4.13422	0.00	0.36	—0.36	0.0	8.7	—8.7	22.4	...	—22.4	—7.0	—15.4
7	Apr. 16	4.21177													
		4.21177													
		4.21177	4.21240	4.21204	0.36	0.63	—0.27	8.6	14.9	—6.3	16.0	...	—7.4	5.6	—13.0
8	Apr. 22	4.08371													
		4.08365													
		4.08368	4.08473	4.08371	1.02	1.05	—0.03	25.0	25.8	—0.8	27.6	...	—2.6	4.9	—7.5
9	Apr. 30	4.17586													
		4.17588	During the run, the electrolyte became cloudy on dilution. Not included in the mean.												
		4.17587	4.17741	4.17651	0.90	1.54	—0.64	21.5	36.8	—15.3	27.2	...	...	...	...
10	May 4	4.14317													
		4.14308													
		4.14312	4.14320	4.14391	—0.71	0.08	—0.79	—17.1	2.0	—19.1					
11	May 7	4.08103													
		4.08087													
		4.08095	4.08097	4.08147	—0.52	0.02	—0.54	—12.7	0.5	—13.2					
12	May 15	4.09390													
		4.09387													
		4.09389	4.09478	4.09386	0.92	0.90	0.02	22.5	22.0	0.5	15.9	...	6.6	12.8	—6.2
	Mean							12.1	17.7	—5.6	19.5	6.7	—7.4	4.9	—12.3
	Prob. error of 1 observation							7.5	4.5	3.4	3.8	...	5.7	3.4	..
	Prob. error of the result							3.3	2.0	1.6	1.7	...	2.5	1.6	..

Same electrolyte was used in both of these runs and the acidity was not tested. Obviously something was wrong, so these two results are not included in the mean.

discordant with all the other runs and were therefore omitted in taking the average. In Run 9 the electrolyte became turbid on dilution before and during the run and for this reason the run was also questioned and not used for calculation.

The results are not as conclusive as desired, but, correcting for the inclusions, they show an agreement of the anode loss and the cathode gain to within 7.4 parts per 100,000. In this method there is considerable manipulation and it must be remembered that any loss of silver either at the anode or cathode would mean an increase in the anode loss and a decrease in the cathode gain, so that this figure is a maximum. The calculated probable error of the result is 3.3 parts in 100,000, but any loss of finely divided silver which would pass unseen through the Neubauer crucible would always be a loss in the same direction and would not appear in the calculation of the probable error. The cathode deposit is actually greater than the anode loss, but, for some unknown reason, the inclusions in deposits in this type of voltameter as operated are much larger than in the platinum cup voltameter. The results also indicate that the pure silver deposited in this voltameter is greater than in the platinum cup voltameter by 4.9 parts per 100,000. The probable error of the result is calculated to be 1.6 parts and the difference observed has therefore little significance. A curious feature in the result is the large amount of inclusion in the deposits in this form of apparatus as is shown in Table III and the correspondingly large actual deposits obtained. To investigate this effect, some runs were made using a highly polished silver cup as the cathode, scraping down the deposit before weighing. The samples thus obtained do not show such abnormal inclusions.

II. Deposits on a Silver Cup.

These runs were made at the Bureau of Standards at Washington in coöperation with Mr. Vinal and were also used to determine the inclusions between the crystals and the cup and for two determinations of the value of the inclusions by the flame method.[1]

The silver cups were similar in size and shape to the platinum cups of the standard voltameters and were highly polished with rouge, then with a felt wheel and finally with broadcloth mounted on the rotating spindle of a lathe. They were soaked in caustic potash solution, water, silver nitrate solution, and were then washed and heated to 160° before use. The anodes and porous pots were identical with those used in the platinum cup voltameter. After the run the silver was scraped down while wet by means of a small silver "hoe" which was always weighed with the cup.

The runs are given in Table II and the inclusions in the deposits are

[1] Vinal and Bovard, *J. Am. Chem. Soc.*, **38**, 496 (1916).

TABLE II.

Run No.	Date, 1915.	Deposit in Princeton Pt. cups. G.	Deposits in Bureau of Standards voltameters. Large. G.	Deposits in Bureau of Standards voltameters. Small. G.	Detached deposit in silver cups. G.	Average of platinum cups. G.	Deposit on Pt. minus deposits on silver. Mg.	Deposit on Pt. minus deposits on silver. Pts. per 100,000.	Inclusions on Ag cups. Pts per 100,000.	Inclusions on Pt cups. Pts per 100,000.
13	May 26	4.05338	...	...	4.05343					
		4.05326	...	...	4.05349					
							Deposits not detached from silver cups			
		4.05332	...	...	4.05346	4.05332	—0.14	—3.5	..	...
1B	June 24	...	...	...	4.37476					
		...	...	...	4.37460					
							Deposits detached from silver cups			
		...	4.37507	4.37500	4.37468	4.37503	0.35	8.0	9.84	...
2B	July 7	...	4.18013	4.18013	4.17926					
		...	4.18009	4.18013	4.17968					
							Deposits detached from silver cups			
		4.18017	4.18011	4.18013	4.17947	4.18014	0.67	16.0	7.15	...
3B	July 19	4.36827	4.36829	...	4.36807					
		4.36830	4.36819	...	4.36779					
							Deposits detached from silver cups			
		4.36829	4.36823	...	4.36793	4.36826	0.33	7.5	10.17	...
5B	Aug. 9	4.22600	...	...	4.22586					
		4.22592	...	...	4.22501					
							Deposits detached from silver cups			
		4.22596	...	...	4.22544	4.22596	0.52	12.3	7.18	...
6B	Aug. 16	4.20758	4.20768	4.20780	4.20695					
		4.20764	4.20749	4.20733	4.20683					
							Deposits detached from silver cups			
		4.20761	4.20758	4.20756	4.20689	4.20758	0.69	16.7	2.06	...
Mean of runs where deposits in silver cups were detached								12.1	7.3	6.7
Prob. error of result								±1.3	±1.5	...

given in Table IV. The results show that the inclusions in deposits on silver are more variable, but not greatly different from the inclusions in deposits on platinum. They do not explain, however, the very high inclusions in the cathode gain voltameter. An explanation has not been obtained for the difference between the deposits on platinum and the scraped down deposits on silver. The discrepancy seems to indicate that a loss of silver has occurred. No silver was recovered, however, when the electrolyte and washings were passed through a filter paper. In Run 13 in the table, in which the silver was not scraped down, there was an excess deposit on the silver cathode of 3.5 parts per 100,000.

III. Inclusions in Electrolytic Silver.

The question of the inclusions in the electrolytic silver as deposited in the silver voltameter has received considerable attention during the last few years. The first to consider it seriously were Lord Rayleigh and Mrs. Sedgwick[1] in 1884, but since their time our advance in knowledge of the silver voltameter has materially increased the purity of the silver deposited so that their results are largely of historical interest. These authors did, however, develop two of the methods which have been most frequently used in determining the inclusions; namely, the method of direct analysis of the deposited silver by dissolving it in nitric acid and weighing as chloride or bromide, and also the method of heating the deposit to a high temperature to remove any volatile impurity.

The second method employed by Lord Rayleigh and Mrs. Sedgwick is the simplest to carry out and is the one which has been most frequently used. In the best recognized voltameter practice, the properly washed silver deposit is heated to 160° in the platinum dish in which it was deposited. After the mass of the deposit has been obtained in this way, it has been found that a further heating to a red heat generally occasions a slight loss in weight which is attributed to a volatilization of occluded electrolyte; that is, to a loss of water and the volatile part of the silver nitrate occluded in the deposit. There is, of course, a question as to whether all of the water and volatile products can be removed at dull red heat, but it is not possible to go beyond this temperature without seriously alloying the silver and platinum.[2] The heating has been mostly done over a free flame but in some cases an electric furnace has also been employed.

The weighing may be made very precise, but at best all of the errors fall on a small difference of about 5 parts in 100,000 of the silver. Since the silver and dish are weighed and heated together and the dish is ordinarily over ten times the weight of the silver, the information gained consists really in an interpretation of a loss of some 5 parts in a million of

[1] *Phil. Trans.*, **175**, 411 (1884).

[2] Vinal and Bovard, Bur. Standards, *Bull.* **13**, 152 Reprint No. 271 (1916).

this system when heated from 160° to red heat, and all of the errors fall on this small difference. It is obvious, therefore, that a single determination has no real significance, in fact, it is necessary to exercise caution in drawing conclusions from a series of determinations, but since a number of different workers have tried this same method it is of interest to collect in the form of a table the average results of the different investigations together with the number of determinations and an idea of the variations. Only the results on deposits which may be regarded as corresponding to accepted voltameter practice have been taken into account in the following table:

Year.	Observers.	Mean loss in wt. Parts per 100,000.	Error of a single determination.	Extreme values. Min. loss.	Extreme values. Max. loss.	No. of determinations.
1902	Richards and Heimrod[1]	18.0	5.3	—3	—30	12
1906	Van Dijk[2]	0.3	0.05	+2	— 6	9
1912	Boltzmann[3]	2.3	1.5	—3	— 8.7	19
1915	Jaeger and von Steinwehr[4]	0.8	1.0	+2	— 5	18
1915	Richards and Anderegg[5]	15.0	5.7	—3.9	—36.5	31
1915	Vinal and Bovard[6]	4.0	1.5	0	— 7.9	25

There is no agreement in the results in the first column, which gives the average result for each investigation. There is a very marked difference between the values obtained by Richards and his co-workers and all other investigations, but even if we exclude the results of these two investigations, the remaining four results do not show an agreement within the probable error of a determination. Vinal and Bovard[7] have evidence to show that a momentary heating at incipient red heat removes at least 90% of impurities which can be removed at this temperature so that the time of heating does not appear to account for any marked differences in results by this method nor is there a measurable inclusion of electrolyte between the silver crystals and the dish as will be shown later. The inclusions may vary but the work of Hulett and Duschak[8] indicated that the inclusions are uniformly distributed throughout the silver crystals. The crystals of the deposits vary markedly in size depending on the current density and especially on the roughness and previous history of the platinum surface on which they are deposited. Duschak and Hulett[9] found, on heating electrolytic silver in a vacuum, that little gas was given off

[1] *Z. physik. Chem.*, **41**, 323 (1902).
[2] *Ann. Physik*, **19**, 266 (1906).
[3] *Sitzb. Akad. Wiss., Wien*, **121**, 1062 (1912).
[4] *Z. Instrumentenk.*, **35**, 226 (1915).
[5] *J. Am. Chem. Soc.*, **37**, 7, from Table III and V (1915).
[6] *Loc. cit.*, p. 506.
[7] *Loc. cit.*, p. 509.
[8] *Trans. Amer. Electrochemical Soc.*, **12**, 257 (1907).
[9] *Loc. cit.*

at 400° and that not all of the volatile constituents were eliminated until the silver was melted. This point is also confirmed by the fact that the values subsequently obtained by the tin method are greater than the values determined on similar deposits by the flame method by 2 to 3 parts in 100,000.

One would hardly expect to get all of the volatile inclusions out of these silver crystals by heating momentarily to a dull red heat (about 600°) which is some 350° below their melting point, so that with different sized crystals one could readily understand variable results by the heating method. On the whole then, it would seem that these investigations clearly establish the existence of inclusions and that perhaps the values obtained are minimum values. Furthermore, an interesting source of error in this method has lately been discovered.[1] There is always more or less alloying of the silver and platinum, the extent of which depends not only on the temperature employed but also noticeably on the time of heating at a given temperature. When this silver is removed by nitric acid a black stain of platinum black is left on the dish which has exceptional powers of retaining volatile impurities which are not measurably removed up to 200° but are removed at a red heat. This stain is often scarcely visible and very difficult to remove, so that in the regular voltameter practice such a dish might give nearly normal results as to the mass of the silver deposited, but on heating the system to red heat there would result a loss many times that of the volatile impurities from the silver deposit. This source of error might account for the Harvard results. Richards and Anderegg[2] have published a note in which they admit that they have not taken precautions against this source of error. However, the loss of 15 parts in 100,000 observed by these investigators was supported by their other work where they dissolved the silver from the cup and precipitated it and weighed it as a the chloride, employing all of the precautions used in the Harvard atomic weight work. Seven such determinations gave inclusions varying from 10.6 to 17.6 parts in 100,000 with an average result of 14.1 and probable error of 1.8 for a single determination.

Furthermore, these authors made some determinations in which the silver crystals were detached from the platinum dish with a platinum spatula and then heated in a quartz crucible. A loss of 17 parts in 100,000 was observed when 7.22 grams of such crystals, obtained from several runs, were heated to dull redness. Fearing a slight loss of silver by volatilization, these authors heated some detached crystals in a quartz test tube, which was also evacuated, so that any volatilization of silver could be avoided. Using 10.1 and 9.8 g., the losses observed were 13.5 and

[1] Vinal and Bovard, *J. Am. Chem. Soc.*, **38**, 476 (1916).

[2] *J. Am. Chem. Soc.*, **38**, 2044 (1916).

11.5 parts in 100,000, respectively. The scraped crystals may have removed some of the platinum black, if present, but one would not expect that to be much of a factor. There are here two independent methods and an important variation of the heating method giving average results which are in remarkable agreement. The average of all of the Harvard investigations seems to show 15 parts of inclusions in 100,000 parts of silver, but this value is given no support by any of the numerous and careful investigations on this question.

It has been seen that the heating method gives us only the conclusion to be obtained by interpreting a small loss which includes all of the errors of experimentation and is seen to be beset with other difficulties. The method of analyzing the deposited silver for total silver is again an attempt to gain our information from a small difference which contains all of the errors of manipulation. Although the knowledge and experience in this particular kind of analysis is exceptional, nevertheless, for the purpose in hand the method is an unfavorable one. In this laboratory the problem has been attacked from an entirely different standpoint, namely, to attempt to isolate the impurities and measure them directly. The first attempt to accomplish this was made by Hulett and Duschak,[1] who heated the detached crystals in an evacuated tube attached to a manometer. This experiment gave some interesting information, but it was recognized that heating the silver crystals in a glass tube to 600 or 700° also drove off water vapor and probably a little carbon dioxide from the glass itself, so that later the method was improved[2] by dissolving the silver crystals in molten tin where a liquid alloy was formed and all impurities other than metals were expelled. This was all done in a vacuum where the tin was kept in a molten state and the apparatus thoroughly pumped out before the silver was dissolved, so that there were present no volatile constituents from the glass or materials other than from the silver under consideration. The inclusion predominant in electrolytic silver is naturally silver nitrate solution. It was found by Laird and Hulett and also confirmed by a few experiments in the present work that molten tin reduces silver nitrate quantitatively to nitrogen. It was then a problem of determining the water and nitrogen which was a comparatively simple matter. The results found for water were fairly consistent, being about 4 parts to 100,000 parts of the crystals as deposited from the best silver nitrate solution, but the residual gas taken as nitrogen and calculated to silver nitrate was surprisingly large. This was explained when it was found that there was always present a trace of organic matter, even when taking the greatest precautions with the water, solutions and all manipulations. On dissolving the silver in the tin, not only water

[1] *Trans. Am. Electrochem. Soc.*, **12**, 257 (1907).

[2] Hulett and Laird, *Ibid.*, **22**, 351 (1912).

and nitrogen, but a little organic matter was liberated as a vapor or gas. This complicated the problem but by providing the apparatus with a little copper oxide which would be glowed by an electric current, the gas phase could be made to consist of a mixture of water, carbon dioxide and nitrogen. The water was condensed completely when desired by surrounding a little side tube with solid carbon dioxide and the carbon dioxide was condensed by liquid air, leaving nothing but nitrogen in the gas phase. Unfortunately, this method was not developed until near the end of their work, but 8 determinations on silver deposits obtained with their best solutions and conditions gave 4 parts of water, 0.5 part of silver nitrate and 0.37 part of carbon dioxide, making a total of not quite 5 parts of inclusions per 100,000 of the silver crystals with a probable error of 1.3 parts. In the present work, the method of Hulett and Laird was adopted, but a new form of apparatus was devised to measure the liberated inclusions. It was found in the course of the work that molten tin slowly reduces water vapor to hydrogen as will be shown later and this phenomenon most likely accounts for a portion of the oxidizable gases found in the previous work.

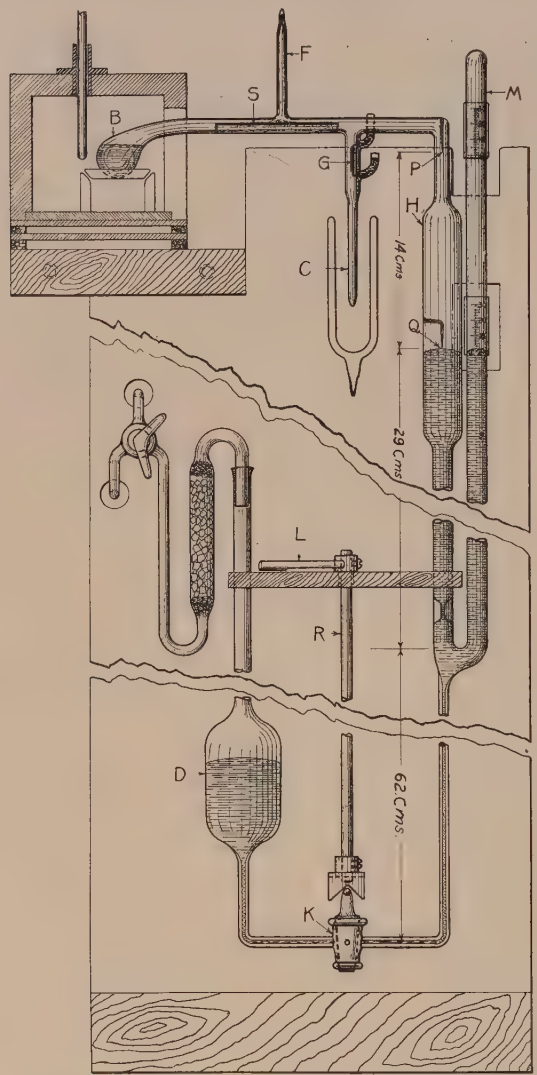
Richards and Anderegg[1] have suggested that there is an opening of cells in the crystals in detaching them from the dish. These authors washed their dish and detached crystals with a little water and found evidence of a small amount of silver in this wash water. But their experiments in determining the inclusions on detached crystals showed, within the experimental error, as large inclusions as the experiments on the undetached crystals. We attacked this question in a different way.[2] By measuring the increase in conductivity of the water before and after stripping, it was shown that less than 0.2 part of silver nitrate per 100,000 was liberated in this manner. This result is a maximum value, as not only the silver nitrate but any other cause of increase of conductivity would be included in the result. Consequently, the amount of silver nitrate liberated by detaching the crystals is very small and does not affect the value of the inclusions determined by the tin method to more than one or two parts per 100,000, even if calculated to a 10% solution. Hulett and Vinal[3] found that silver measurably dissolves in water when in contact with platinum due to the electrochemical action. Silver seems to go into solution as ions and equivalent of hydrogen is discharged into the platinum. This phenomenon may account for some of the silver found by Richards and Anderegg in the wash water after stripping the silver crystals from the platinum cup.

[1] *J. Am. Chem. Soc.*, **37**, 10, 18 (1915).

[2] Hulett and Vinal, *Jour. Phys. Chem.*, **19**, 189 (1914); Vinal and Bovard, *J. Am. Chem. Soc.*, **38**, 511 (1916).

[3] *Jour. Phys. Chem.*, **19**, 173 and *J. Am. Chem. Soc.*, **38**, 510 (1916).

A. **Apparatus.**—The apparatus used to determine the magnitude and composition of the inclusions is shown in the accompanying diagram. It is made of Jena 16^{III} glass, all the parts being fused together. The only stopcock was in the manometer and in a position such that the pressure of the mercury at that point was always greater than one atmosphere. It was lubricated with graphite so as to avoid the danger of contaminating the mercury. The tin was contained in the bulb B, which had a capacity of 10 cc. and was heated in the electric furnace. The weighed sample of silver was placed in the platinum boat S by introducing it through the tube F, which also served as a connection to the mercury pump and later to determine the volume of the apparatus. The slender tube C could be immersed in solid carbon dioxide or in liquid air and served in the analysis of the gases by fractional condensation. The copper oxide glower G was used to oxidize the gases evolved on dissolving the silver in molten tin. It was made as follows: A platinum wire of 0.1 mm. diameter was slipped through a drawn quartz tube of 0.4 mm. diameter and two heavier platinum wires 0.3 mm. diameter were welded to the ends of the smaller wire. The quartz tube was wound with 0.02 mm. copper wire. The larger platinum wires were then sealed through the glass tube and a mercury seal fused on the outside to prevent leakage. This seal was found necessary as the slightly different coefficients of expansion of the platinum and the Jena 16^{III} glass caused



a very slow leakage before the seal was used. The glower had a resistance of 1.2 ohms and required 2.5 amperes to heat it to redness in air. Before use, the coil was glowed in air until the copper became coated with an adherent coating of copper oxide and was thoroughly glowed while pumping out the apparatus.

The pressure was measured by means of a manometer of special construction. It was advantageous to have the volume of the apparatus constant and this was done by slowly raising the mercury level in H until it touched a sharp glass point P, which was fused to the glass, and then measuring the height of the mercury in the manometer tube *M*. The point P was ground so as to be more plainly visible. A telescope was inclined at such an angle that not only the point itself was visible, but also the reflection of the point in the mercury, and by raising the mercury slowly until the reflection and pointer just met, as viewed in the telescope, the height of mercury could easily be controlled and read to less than a hundredth of a millimeter. The apparatus contained two glass pointers P and Q. In this form of manometer the mercury ascended just before measuring the pressure and thus eliminated the error due to the difference in the form of a rising and a falling meniscus. The height of the mercury was measured with reference to a glass scale securely fastened to the back of the manometer tube. The divisions on the scale were 0.472 mm. and the reading was obtained to fiftieths of one of these divisions by means of a telescope with a micrometer eye piece placed three feet away so as to avoid parallax. By calibrating the micrometer eye piece in terms of the scale divisions, the readings of the meniscus were made to a fiftieths of a scale division or to 0.01 mm. In this way the readings were always made with reference to a scale rigidly fixed to the manometer tube and not dependent on bringing the apparatus back to the same position after tilting to dissolve the silver in the molten tin. A sharp meniscus was obtained by placing a Nernst glower in back of the scale and then lowering a slotted plate of hard rubber until the shadow just met the top of the miniscus, thus giving a very sharp and constant outline as viewed through the micrometer telescope. The height of the mercury was adjusted by means of the stopcock K, which could be accurately controlled by means of the level L and the rod R. The lower end of R was attached to a bar which was V-shaped so as to fit over the stopcock. The cock was placed one meter below the top ground glass pointer so that when the apparatus was evacuated the pressure of the mercury was still greater than one atmosphere. The mercury in the reservoir D could be opened to the atmosphere or subjected to pressure and thus the height of the mercury varied at will. Finally the complete apparatus was mounted on a board that was hinged to a slate block cemented to two brick piers and having three nickel points in the bottom

so that it returned to the same level after tilting. Readings were always duplicated by adjusting the mercury twice to contact with the point, taking a reading of the mercury level after each adjustment.

The electric furnace used to heat the tin was made of asbestos board in the shape of a box 10 cm. on a side, the walls having air spaces to obtain better heat insulation. It was made in two parts, a bottom part to which was fastened a clay tripod to support the bulb B and a top part, one side of which was slotted so that it could be slipped over the tube connecting the bulb B with the manometer. One side of the furnace was made of three sheets of mica so that the bulb B could be easily watched during the operation of dissolving the silver. The heating was accomplished by means of spirally wound nichrome ribbon fastened on all sides of the box. The furnace had a total resistance of 16 ohms and a current of 4.1 amperes maintained a very constant temperature of 500°. The temperature was measured by means of a nickel-nichrome thermocouple and a millivoltmeter.

In order to make the calculations, the volume and temperature of the apparatus must be known. The various parts of the apparatus are, however, at different temperatures and so after the run the volume of nitrogen at atmospheric pressure and room temperature needed to fill the apparatus under working conditions was determined. This was accomplished with the aid of a special form of buret which gave the volume with the requisite degree of accuracy. The volume of the apparatus under working conditions was 9 cc. when using the top point and 47 cc. when using the bottom point.

B. **Method of Determination.**—The impurities which could exist in electrolytic silver as deposited are water, silver nitrate, hydrogen and, perhaps dust or colloidal matter. The gases liberated when the deposit is dissolved in molten tin are therefore limited to water vapor, nitrogen, carbon dioxide, hydrogen and, perhaps, hydrocarbons. It is found experimentally that by far the greater part consists of water vapor and that in good deposits all of the other volatile constituents amount to less than one part in 100,000 of the deposit.

Laird and Hulett[1] found that there was present a certain amount of oxidizable gas. We have found that molten tin reduces water vapor to a slight extent and that their oxidizable gases were to a certain extent formed in this way by the reducing action of the tin. The method of analysis was therefore to dissolve the silver in the tin, burn all oxidizable gases to CO_2 and H_2O, and then to analyze the gas mixture by fractional condensation, using solid carbon dioxide (—78°) and liquid air (—180°). The vapor pressure of water is less than 0.001 mm. at —78° and that of

[1] *Trans. Amer. Electrochem. Soc.*, **22**, 351 (1912).

carbon dioxide is less than 0.001 mm. at —180°, so that only the nitrogen would be uncondensed at this latter temperature.

It was found by Laird and Hulett that silver nitrate is reduced quantitatively by molten tin and this point was also tested experimentally in our apparatus. In one of the experiments 15 mg. of silver nitrate, placed in a small boat of pure silver, were introduced into the apparatus. On dissolving in the molten tin red-brown fumes of nitrogen dioxide were seen. After ten minutes the color had entirely disappeared and the pressure had decreased to half of its original value. The gas was not condensable at the liquid air temperature. Calculation of the final observed pressure to silver nitrate gave an agreement with the weight of salt taken considerably better than that demanded for the present work.

The method of analysis as finally worked out was as follows: The sample under investigation was weighed and heated to 160° for an hour in an electric furnace. It was then introduced into the platinum boat S through the tube F by means of a clean glass funnel made so as to fit very snugly over the tube F. A piece of Jena 16^{III} glass tubing of the same diameter as F was drawn down to a thick capillary and sealed on to F with a hand blow pipe. This tube was then connected to the Töppler pump by lead tubing and Khotinsky cement and the apparatus carefully evacuated. The tin was heated to 500° and the copper oxide glower heated to redness. The mercury was run down to the bottom point, then back again to the top point and the apparatus was maintained in this condition for an hour so that all gases given off by the tin or glower or the heated parts of the glass were removed. In the last runs a phosphorus pentoxide bulb was inserted in the line near the apparatus and the pressure was reduced well below 0.01 mm. pressure. The connecting capillary was then sealed off by means of a hand blow pipe and the copper oxide glower allowed to cool. Initial readings were then taken on the top scale with the tube C at room temperature, —78° and at —180°. With the solid CO_2 on, the whole apparatus was tilted and jarred so that the silver ran down into the molten tin, in which it was immediately dissolved. The apparatus was then returned to its original position and allowed to stand for an hour. The readings were constant after fifteen minutes, but more time was allowed in order to be sure that equilibrium had been attained.

The glower was now heated to redness, cooled and readings taken with the condenser tube at —78° and then at —180°. The glower was again heated to ascertain if all of the gas had been oxidized and the readings at —180° again taken. The mercury was then taken to the lower point and the pressure determined at room temperature and with the condenser tube at —78°. The volume of this lower point was so chosen that the pressure of the water was well below the saturation pressure. The vol-

ume of the apparatus to the top point was now determined by connecting the filed end of the capillary to the buret previously mentioned and measuring the volume of nitrogen necessary to fill the apparatus with the tin still melted and the conditions the same as during the run. Allowance was made for the small pressure already in the apparatus. One batch of tin amounting to about 60 g. was used for about five successive samples of silver. A complete determination occupied about five hours.

C. **Results.**—The results are given in Tables III, IV and V. The cathode gain deposits used for Table III were the samples obtained in the cathode gain and anode loss apparatus. The deposits on silver used for the results in Table IV were those obtained by scraping down the silver cups for the runs given in Table II. The samples for the determination of the inclusions in deposits on platinum in Table V were made at the Bureau of Standards through the kindness of Mr. Vinal. They were deposited in the standard platinum cup voltameters, the electrolyte having been prepared at Princeton and fused at Washington.

Unfortunately, the discovery of the fact that the tin reduced water vapor did not come until most of the runs had been made. In the first runs, no particular attention was paid to obtaining a high vacuum and it was thought that if the initial readings were used to correct the final readings, that good results would be obtained. As a result, in several of the first runs, the readings obtained at —180° after tilting and glowing was actually less than the initial reading. This behavior was very puzzling until it was discovered that water vapor was reduced by molten tin. The readings before tilting were taken some time after the glower had been in operation and it is very likely that some of the water vapor was reduced to hydrogen and that after tilting this hydrogen was oxidized to water and gave a lower reading at liquid air temperature. For this reason, the nitrogen was not calculated in any of the runs previous to July 1st, except in Run 4, where the record of the experiment showed that a good vacuum had been obtained. The amount of nitrogen in the deposit is very small and the value that would be calculated would be greatly in error. The amount of CO_2 and water is so much larger than this error, however, that this small change does not appreciably alter their results. The reduction of the liberated gases by molten tin is very clearly shown by the following record, the figures given having been obtained after the regular procedure had been completed:

Time.	Pressure in mm. of mercury.	Temp.	Procedure.
2.18	0.07	—180°	after tilting and glowing
2.53	1.59	—180°	liquid air removed and replaced 2.51
2.56	0.07	—180°	glower heated to redness and cooled
3.07	0.06	—180°	liquid air not removed
3.55	2.64	—180°	liquid air removed and replaced 3.53
4.22	3.63	—180°	liquid air removed and replaced 4.20
4.26	0.08	—180°	glower heated to redness and cooled

The results given in Tables IV and V indicate that the inclusions in deposits on platinum are more constant than in those on silver and slightly less in amount. The mean value of the inclusions in the platinum cup samples is found to be 6.74 parts per hundred thousand and this is 2.7 parts higher than the values obtained at the Bureau of Standards on similar deposits by the method of heating the deposit to incipient redness.[1] One sample on platinum which had been ignited showed inclusions to the extent of 2.1 parts per hundred thousand, so that this is also evidence that heating the deposit to redness does not expel all of the inclusions.[2] The reproducibility of the method employed is shown in the following table:

		Parts per hundred thousand.				
Sample.	Run. 1916.	H_2O.	CO_2.	$AgNO_3$.	Total not counting $AgNO_3$.	Discrepancy.
2B deposit on silver....	No. 1 Apr. 20	5.42	1.66	?	7.08	0.12
	No. 2 June 26	5.82	1.38	?	7.20	
3B deposit on silver....	No. 3 Apr. 28	9.95	0.81	?	10.76	1.40
	No. 8 May 15	8.81	0.46	?	9.36	
5B deposit on silver....	No. 2 Apr. 26	5.85	0.93	?	6.78	0.19
	No. 26 July 11	5.65	0.94	0.73	6.59	
				Mean discrepancy,		0.67
8 cathode gain.....	No. 20 June 29	19.4	1.65	?	21.0	9.8
	No. 22 July 3	29.8	1.98	1.67	30.8	
9 cathode gain.....	No. 17 June 27	27.6	0.84	?	28.4	2.4
	No. 19 June 28	25.3	0.77	?	26.0	
				Mean discrepancy,		6.1

Thus in a deposit of moderate inclusions, a determination to 1 part in a hundred thousand can be obtained.

Only five determinations of the silver nitrate in a normal deposit were obtained, giving an average value of 0.73 part per hundred thousand. The water in these same deposits is found to be 6.25 parts so that it seems likely that the silver nitrate present exists in an approximately 10% solution in the crystals.

		Parts per hundred thousand.	
Sample.	Run.	Water found.	$AgNO_3$ found.
Deposit on platinum.....	No. 21	4.93	0.75
Deposit on platinum.....	No. 23	6.10	1.19
Deposit on platinum.....	No. 24	6.54	0.27
1B deposit on silver.....	No. 4	8.03	0.73
5B deposit on silver.....	No. 26	5.65	0.73
	Mean,	6.25	0.73

The carbon dioxide must have come either from dust or from silver carbonate or some other organic colloid attracted to the cathode during

[1] Vinal and Bovard, Bur. Standards, *Bull.* 13, 160 (1916).

[2] *Loc. cit.*, p. 12.

TABLE III.—INCLUSIONS IN THE CATHODE GAIN DEPOSITS.

Sample.	Run No.	Date. 1916.	Mm.³ N. T. P. per 1 g. silver. Increase at −79°.	Condensed −79° to −180°.	Uncondensed at 180°.	Total H_2O.	Parts per hundred thousand. H_2O.	CO_2.	$AgNO_3$.	Total inclusions.
Run No. 5 Apr. 1, 1915.....	25	July 3	1.59	1.09	0.496	141	11.3	0.31	0.75	..
Run No. 6 Apr. 9, 1915.....	18	June 27	..	4.59	?	268	21.5	0.90	?	..
Run No. 7 Apr. 17, 1915.....	14	June 24	..	9.60	?	178	14.3	1.68	?	..
Run No. 8 Apr. 22, 1915.....	20	June 29	..	8.41	?	241	19.4	1.65	?	..
Run No. 8 Apr. 22, 1915.....	22	July 3	6.09	4.99	1.10	370	29.8	0.98	1.67	..
Mean of Run No. 8.....							24.6	1.32	1.67	..
Run No. 9 May 1, 1915.....	17	June 27	..	4.30	?	344	27.6	0.84	?	..
Run No. 9 May 1, 1915.....	19	June 28	..	3.93	?	315	25.3	0.77	?	..
Mean of Run No. 9.....							26.5	0.80	?	..
Run No. 12 May 19, 1915....	15	June 24	..	4.20	?	187	15.1	0.82	?	..
Average of runs.....							18.9	0.97	1.21	21.1
Prob. error 1 obs.....							±4.1	±0.32	±0.44	..
Prob. error result.....							±1.7	±0.13	±0.36	..

TABLE IV.—INCLUSIONS IN DEPOSITS ON SILVER CUPS.

Sample.	Run No.	Date, 1915.	Mm.³ N. T. P. per 1 g. silver. Increase at −79°.	Condensed −79° to −180°.	Uncondensed at −180°.	Total H_2O.	Parts per hundred thousand. H_2O.	CO_2.	$AgNO_3$.	Total inclusions.
Run 1B June 24, 1915.....	4	Apr. 29	6.00	5.52	0.485	99.6	8.03	1.08	0.73	..
Run 2B July 9, 1915.....	1	Apr. 20	..	8.47	?	67.3	5.42	1.66	?	..
Run 2B July 9, 1915.....	16	June 26	..	7.08	?	72.4	5.82	1.38	?	..
Mean of Run 2B.....							5.62	1.52	?	..
Run 3B July 20, 1915.....	3	Apr. 28	..	4.14	?	123.8	9.95	0.81	?	..
Run 3B July 20, 1915.....	8	May 15	..	2.38	?	109.3	8.81	0.46	?	..
Mean of Run 3B.....							9.38	0.64	?	..
Run 5B Aug. 9, 1915.....	2	Apr. 26	..	4.79	?	72.6	5.85	0.93	?	..
Run 5B Aug. 9, 1915.....	26	July 11	..	4.83	0.481	70.6	5.65	0.94	0.73	..
Mean of Run 5B.....							5.75	0.93	0.73	..
Run 6B Aug. 18, 1915.....	9	May 21	..	1.82	?	21.1	1.70	0.36	?	..
Average of runs.....							6.09	0.91	0.73	7.73
Prob. error 1 obs.....							±1.97	±0.30	..	..
Prob. error result.....							±0.88	±0.13	..	..

TABLE V.—INCLUSIONS IN DEPOSITS ON PLATINUM.

Sample.	Run No.	Date. 1916.	Mm.³ N. T. P. per 1 g. silver. Increase at −79°.	Condensed −79° to −180°.	Uncondensed at −180°.	Total H_2O.	Parts per hundred thousand. H_2O.	CO_2.	$AgNO_3$.	Total inclusions.
Pure electrolyte baked	7	May 13	...	2.71	?	19.7	1.59	0.53	?	2.12
Electrolyte contaminated with filter paper	11	June 16	61.0	53.4	7.65	198.0	15.91	10.46	11.59	37.96
Large crystals from very acid solution	27	July 11	2.87	0.99	1.88	greater than (434)	(35.0)	0.19	0.23 Nitrogen	735.0
Pure electrolyte Sample A	10	June 14	...	1.46	?	70.7	5.69	0.29	?	..
Pure electrolyte Sample B	12	June 23	...	1.76	?	69.0	5.55	0.35	?	..
Pure electrolyte Sample C	13	June 23	...	2.33	?	65.8	5.37	0.45	?	..
Pure electrolyte Sample D	21	July 2	2.31	1.82	0.494	61.2	4.93	0.36	0.75	..
Pure electrolyte Sample E	23	July 3	4.72	3.94	0.787	75.8	6.10	0.29	1.19	..
Pure electrolyte Sample F	24	July 3	0.91	0.73	0.18	82.7	6.54	0.14	0.27	..
Mean of results from normal samples							5.69	0.31	0.74	6.74
Prob. error 1 obs							±0.38	±0.07	±0.17	..
Prob. error result							±0.16	±0.03	±0.07	..

electrolysis. It is, however, a very small part of the total value and has an effect much smaller than one part in a hundred thousand For, expressed in CO_2, the value given must be considerably greater than the actual carbonaceous inclusions from which the carbon dioxide was obtained.

Run 11 was of a deposit which had been precipitated from an electrolyte contaminated with filter paper and shows considerable inclusions, especially of organic material. It is well known that a deposit from such a solution is abnormally high and this one result conforms to the theory that colloidal silver is produced by the filter paper extract which, although itself a negative colloid, acts as a protective colloid and is carried to the cathode with the positively charged colloidal silver.[1] Run number 27 was made on a deposit that had been precipitated from a solution that was very strongly acid. It also shows very high inclusions with a very large amount of water and nitrogen. The amount of water could not be determined because the pressure of the water even at the lower point was greater than the saturation pressure at this temperature.

IV. Value of the Electrochemical Equivalent.

The International Electrical Conference at London, in 1908, defined the International ampere as the current which would deposit 1.11800 mg. of silver per second under standard conditions.[2] Subsequently, the Bureau of Standards made a series of determinations using an absolute current balance and the same voltameters as were used to obtain the deposits used in the present work. They recommended 1.11804 mgs. per coulomb[3] and this was later revised to 1.11805, not correcting for inclusions.

In this paper the inclusion in the silver as deposited is found to be 6.7 parts per hundred thousand, so that correcting the above value of 1.11805, we get 1.11798 as the value of the electrochemical equivalent of silver. In the present work the anode loss was found to agree with the cathode gain to 7 parts per hundred thousand as a maximum difference, so that this value of the electrochemical equivalent cannot be in error by more than several units per hundred thousand.

Value of the Faraday.

The faraday is the quantity of electricity necessary to liberate one gram equivalent, so that its value depends not only on the electrochemical equivalent but also on the atomic weight. The present international table gives 107.88 as the atomic weight of silver and the corresponding value of the faraday is $\frac{107.88}{0.00111798 \pm 7} = 96496 \pm 7$. But it is of inter-

[1] Rosa, Vinal and McDaniel, Bur. Standards, *Bull.* **9**, 240 (1912).

[2] Report of the London Conference 1908, p. 178.

[3] Bur. Standards, *Bull.* **9**, 367 (1912).

est to consider some of the recent work done on the atomic weight of silver where the procedure is a direct comparison of silver to oxygen (which is taken equal to 16.00 as the basis of atomic weights). This method does not involve any errors in the atomic weight of other elements as would be necessitated by indirect comparison.

Observer.	Procedure.	At. weight of silver.
Richards[1]	$Ag/AgNO_3$ N = 14.010	107.883
Richards and Willard[2]	$LiClO_4/LiCl$ and $AgCl/LiCl$	107.871
Baxter[3]	Ag/I_2O_5 and Ag/I	107.864

The maximum variation here is 19 parts in 100,000 so that the error in our value of the faraday may well center largely on errors in the atomic weight. It is of importance, therefore, to obtain the electrochemical equivalent of other elements with an accuracy comparable to that of silver.

We have Washburn and Bates' Iodine Coulometer[4] where the anode and cathode reactions check exceptionally well. The electrochemical equivalent of iodine was found to be 0.00131502[5] and the ratio of silver to iodine to be 0.85017. The ratio of the present international atomic weights of silver to iodine is $\frac{107.88}{126.92} = 0.84998$, so that the ratio found in the voltameters is greater than that of the atomic weights by 23 parts per 100,000. The inclusion in the silver deposit is 7 parts and the anode loss cathode gain divergence is less than 7 parts, so that it is evident that a very real discrepancy exists between the ratios of the electrochemical equivalents and the atomic weights.

Laird and Hulett have developed a cadmium voltameter,[6] where the cadmium was deposited in mercury, thus eliminating the problem of inclusions. Previous work[7] had shown that the cadmium amalgam could be handled without loss of cadmium. The cadmium voltameters were run in series with silver voltameters and the electrochemical equivalent of cadmium was found to be 0.000581978.

The following table summarizes these electrochemical equivalents and gives the corresponding values of the faraday, using the international atomic weights:

[1] *Carnegie Inst. Publications*, **1907.**

[2] *J. Am. Chem. Soc.*, **32,** 4 (1910).

[3] *Ibid.*, **32,** 32 (1910).

[4] *Ibid.*, **34,** 1341 (1912).

[5] Vinal and Bates, Bur. Standards, *Bull.* **10,** 442 (1914). The iodine coulometer was run in series with silver coulometers under exactly the same conditions as when the latter were run in series with the ampere balance.

[6] *Trans. Am. Electrochem. Soc.*, **22,** 385 (1912).

[7] Quinn and Hulett, "The Atomic Weight of Cadmium," *J. Phys. Chem.*, **17,** 779 (1912).

	Electrochemical equivalent.	International atomic weight.	Corresponding value of a faraday.
Silver voltameter.....	0.00111798	107.88	96496
Iodine voltameter.....	0.00131502	126.92	96516
Cadmium voltameter.....	0.00058198	112.4	96569

These values of the faraday appear to be well within the possible variation of the atomic weights. For example, a direct conparison of the silver and cadmium voltameters indicates the atomic weight of cadmium to be 112.3, taking the atomic weight of silver as 107.88. The generally used value for the faraday is 96540. This number is most likely too high and it may be well to round it off to 96500 with a probable error of from 10 to 20.

V. Summary.

1. A special form of voltameter has been devised and used to determine the agreement between the amount of pure silver deposited at the cathode and dissolved at the anode. An agreement to within 7 parts per hundred thousand corrected for inclusions has been obtained. In the method used any error in the large amount of manipulation would tend to make the divergence greater, so that this figure represents a maximum.

2. An improved form of apparatus has been devised to measure the inclusions in the silver voltameter deposits and an accuracy of one part in a hundred thousand has been obtained.

3. The value of inclusion in deposits on a standard platinum cup voltameter has been found to be 6.7 parts per hundred thousand, giving 1.11798 as the value of the electrochemical equivalent of silver and 96496 as the value of the faraday.

4. The inclusions in deposits on silver are of the same value as those on platinum to within one part per hundred thousand, a value of 7.7 having been obtained.

5. The silver deposited on a silver wire in the special form of apparatus used for the anode loss and cathode gain comparison has been found to contain very large amounts of inclusions. The explanation for this abnormality is not yet forthcoming.

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